

PATENT SPECIFICATION

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(54) PREPARATION OF POLYCHLOROPRENE

(71) We, DENKI KAGAKU KOGYO KABUSHIKI KAISHA, a company organised under the laws of Japan, of 10, 1-chome, Yuraku-cho, Chiyoda-Ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with the preparation of polychloroprene.

Highly viscous polychloroprene which is completely soluble in solvent is especially effective for use as a basic polymer for adhesives.

Further, since it exhibits high loading ability and high strength as a solid rubber, it is an important material. However, such polychloroprene of high viscosity has been produced hitherto only in a low conversion ratio, and a method of its preparation at a high conversion ratio in economical efficiency has been desired.

The conversion ratio referred herein shows how much the added monomer is converted to polymer, and is calculated according to the following formula:

$$\text{Conversion ratio (\%)} = \frac{\text{quantity of monomer converted to polymer}}{\text{quantity of added monomer}} \times 100$$

The use of chain transfer agents including *n*-dodecyl mercaptan (*n*-DDM) in preparing polychloroprene has been known. Up to this time, methods of regulating the viscosity of the polymer to be polymerized by adding to the monomer a chain transfer agent in a single quantity before or at the beginning of polymerization have been used. The greater the amount of chain transfer agent is used, the lower the viscosity of the polymer becomes. A polymer of high viscosity can be obtained by using a small amount of the transfer agent. However, too small amount of the transfer agent gives rise to gelation of the polymer which makes it insoluble in any solvent. Since gel polymer can not be dissolved in a solvent, it is not favorable for use as the basic polymer of adhesives, and moreover when used as a solid rubber it possesses difficulties in processing.

In polymerizing chloroprene to prepare polychloroprene of high viscosity, a chain transfer agent has hitherto been added in a single quantity to the monomer before the beginning of

the polymerization. In such a case, as described in Journal of Applied Polymer Science, vol. 7, pp 675—683, 1963, it is known that when the polymerization is carried out with a chain transfer agent added in a single quantity before the beginning of the polymerization, a violent cross-linking reaction takes place which results in a gelation of the polymer after the conversion ratio has exceeded a certain limit.

Using a decreased amount of the chain transfer agent for the purpose of obtaining polychloroprene of high viscosity gelation takes place while the conversion ratio is still low.

In U.S. Patent Specification No. 3,393,187, a method of producing high molecular polychloroprene is described. In that Specification the polymerization is carried out at a temperature below 22°C in the presence of a chain transfer agent under a critical condition of a conversion ratio of 67 to 73%. In this method, a temperature above 22°C and an arbitrary conversion ratio can not be selected because of the addition of the chain transfer agent in a single quantity.

Thus, such conventional methods of adding the chain transfer agent in a single quantity before the polymerization have not been able to obtain a polychloroprene of high viscosity and of complete solubility in solvent either in an industrially advantageous high conversion ratio or in an arbitrary conversion ratio at a polymerization temperature in a wide range.

The term polychloroprene used in this specification includes a homopolymer of chloroprene and copolymers of chloroprene with other monomers copolymerizable with chloroprene.

According to the present invention there is provided a method of preparing polychloroprene comprising polymerizing chloroprene or a mixture of chloroprene with a copolymerizable monomer at a temperature of from 5° to 55°C wherein *n*-dodecyl mercaptan is present at the beginning of the polymerization reaction and further *n*-dodecyl mercaptan is added during the polymerization reaction in such a way as to prevent gel formation, at least 50% by weight of the total amount of *n*-dodecyl mercaptan being present at the beginning of the reaction. Typically the polymerization is carried out in aqueous alkaline emulsion.

The supplementary addition may be carried out in portions or in a continuous way. A gel-free polymer completely soluble in solvent can be prepared.

The intrinsic viscosity of this polymer attains a remarkable high value, for example 4.43, which has not been achieved by the conventional method of adding the chain transfer agent in a single quantity before the beginning of the polymerization. The solution viscosity of the polymer is also extremely high compared with that of a conventional polymer. Thus, this polymer gives excellent physical properties to the adhesives made of the polymer.

In a preferred embodiment of the invention the polymerization is started in the presence of 0.03 to 0.08 parts by weight of *n*-dodecyl mercaptan for 100 parts of the monomer and during polymerization, from a conversion ratio of 5 to 60%, a further 0.03 to 0.6 parts by weight of *n*-dodecyl mercaptan is added, the polymerization being performed at a temperature from 10° to 55°C, the initial amount being at least 50% by weight of the total *n*-dodecyl-mercaptan added.

The invention is further described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a graph showing the relationship between the conversion ratio, the amount of the *n*-dodecyl mercaptan as chain transfer agent, the viscosity of the polymer, and the occurrence of gel polymer in an aqueous emulsion polymerization of chloroprene at 10°C, with the chain transfer agent added in a single quantity before the beginning of the polymerization.

Figure 2 is a graph similar to Figure 1 in the case of an aqueous emulsion polymerization of chloroprene at 40°C.

Figure 3 is a graph showing the relationship between the intrinsic viscosity and the solution viscosity of polychloroprene.

In the case of adding a chain transfer agent in a single quantity before the beginning of the polymerization, the inventors have learned quantitatively by precise experiments the extent of the viscosity which could be attained at a given conversion ratio, and the limit of the conversion ratio which would give rise to gelation. The results are shown in Fig. 1 and Fig. 2.

Fig. 1 shows the relationship between the conversion ratio and the intrinsic viscosity [η] of the polymer, the relationship between the amount of the chain transfer agent and the viscosity, and the relationship between the conversion ratio and the solubility range of the polymer, in polymerizing chloroprene at 10°C with the chain transfer agent added in a single quantity before the beginning of the polymerization. The ordinate shows the intrinsic viscosity [η] of the polymer in toluene at 30°C. The abscissa shows the conversion ratio. The annexed numerals to the curves are the amount of *n*-DDM by weight percent based on the monomer, and the broken curve shows the boundary of the conversion ratio for safe non-gelling operation.

In Fig. 1, when 0.01% of *n*-DDM based on the monomer is added before the beginning of the polymerization, the intrinsic viscosity [η] is about 6.9 at a conversion ratio of 10%, and with a further increase of the conversion ratio the viscosity increases. At a conversion ratio of 16%, the resulting polymer gels, and at a conversion ratio above this ratio, a solvent-soluble polymer is not produced. When 0.2% of *n*-DDM is used, the conversion ratio can be increased up to 97%, but a polymer having an intrinsic viscosity [η] of only 1.7 is produced. In general, if the conversion ratio is made to proceed approximately to gelation in the industrial production, it is necessary for safe operation that the conversion ratio be held within the limit of about 10% (i.e. within the broken curve of the figure) lower than the gelation point. In the economical production of polychloroprene a higher conversion ratio is desirable. But in the conventional method in which the chain transfer agent is added in a single quantity before the beginning of the polymerization, it is required to hold the conversion ratio, for example, below 35% in order to bring the intrinsic viscosity above 4.5 as shown in Fig. 1. On the other hand, it is observed that at an economical conversion ratio, for example higher than 60%, to obtain a gel-free polymer, a polymer having an intrinsic viscosity [η] lower than 2.6 is obtained. Fig. 2 shows similar relationships to Fig. 1 at a tempera-

ture above 40°C. It is seen that at 40°C a polymer of much lower viscosity than that at 10°C is obtained at the same conversion ratio.

5 According to this invention, highly viscous polychloroprene which is completely soluble in solvent can be prepared at high conversion ratio with an economic advantage.

10 In this invention, *n*-dodecyl mercaptan as chain transfer agent is not added in a single quantity before the beginning of the polymerization, but is added in several portions or is added continuously during the period from the beginning to the end of the polymerization.

15 According to this invention, the polymerization is started with a small amount of *n*-dodecyl mercaptan, relative to the monomer, added before the beginning of the polymerization; and as observed from the relations shown in Fig. 1 and Fig. 2, by adding a small amount of *n*-dodecyl mercaptan immediately before gelation would occur, the gelation is retarded; then the polymerization is made to proceed further and again immediately before gelation would occur a small amount of the transfer agent is added; and such operations are repeated several times.

20 The polychloroprene prepared according to this invention exhibits, as shown in the Examples below, a high intrinsic viscosity $[\eta]$ which is not achieved at that conversion ratio by the conventional method of adding the chain transfer agent in a single quantity. The amount of the chain transfer agent to be added varies according to the polymerization temperature. For example it is necessary that the polymerization be carried out with the addition of *n*-DDM in such a way that the polymer is not produced in the gel area, for example in Fig. 1.

25 The addition of too great an amount of the chain transfer agent at the beginning of the polymerization leads to a too low viscosity. Therefore, a small amount is to be used. For example, when *n*-DDM is used in a polymerization reaction at 40°C, it is preferable that the DDM is added in an amount less than 0.05% based on the weight of the monomer at the beginning of the polymerization in order to obtain an increased viscosity without causing gelation.

30 After the polymerization is started, the chain transfer agent is added to obtain a desired viscosity with the rise of the conversion ratio, while care is taken so that gelation does not take place.

35 In Fig. 1, for example, if 0.01% of *n*-DDM is added at the beginning of the polymerization, gelation will take place when the conversion ratio proceeds to 15%. Therefore, so as to prevent the gelation, it is preferable that the second addition of *n*-DDM is carried out when the conversion ratio has attained about

10 to 12%. In the same manner *n*-DDM is further added. 65

In this way the chain transfer agent is added once before or at the beginning of the polymerization and later at least once during the polymerization. In order to obtain a highly viscous polymer completely soluble in solvent at a high conversion ratio, it is preferable that both the total amount of the chain transfer agent and the amount to be added at one time is as small as possible, and the number of times of addition is as many as possible. 70 75

The more the number of times of addition of the chain transfer agent, the higher is the viscosity and the higher the conversion ratio of the polymer obtained. Especially, it is most preferable to add the chain transfer agent continuously from the beginning to the conclusion of the polymerization. In such a case, the conversion ratio can be made to proceed practically to 100%, and in addition a gel-free polymer can be obtained. 80 85

The polychloroprene of high viscosity obtained according to this invention dissolves completely in solvents containing carbon disulfide and aromatic hydrocarbons such as toluene and, benzene, and is essentially different from a polymer containing even a small amount of gel. 90

Apart from the addition of the *n*-dodecyl mercaptan, the manner of the polymerization and isolation of this polymer is the same as the known method in which alkaline emulsion polymerization is carried out in the presence of a single quantity of chain transfer agent. 95

The *n*-dodecyl mercaptan may be introduced singly into the polymerization system or may be added in an emulsion form. 100

The polymerization may be carried out in a wide temperature range of from 5° to 55°C. At a temperature below 5°C, conventional emulsion polymerization is difficult to carry out. Above 55°C the polymer tends to gel and it is difficult to obtain a highly viscous and completely soluble polymer. 105

From an economic viewpoint, it is desirable that the polymerization is made to proceed to a high conversion ratio. In general, the conversion ratio is desired to be above 40%, but this invention can be applied in a lower conversion ratio. 110 115

This invention may be applied to the homopolymerization of chloroprene and to the copolymerization with a monomer copolymerizable with chloroprene, for example styrene and/or 2,3-dichlorobutadiene-1,3. In the case of copolymerization, the monomer other than chloroprene is preferably not more than 30% of the monomers. 120

The characteristic of this invention consists in that the *n*-dodecyl mercaptan chain transfer agent is added in portions or continuously so that polychloroprene of high viscosity is produced at a high conversion ratio. This poly- 125

mer may be used as a base for adhesives.

The polymer prepared according to this invention may be isolated from the latex by a known method. The resulting polymer may be dissolved in a solvent to prepare an adhesive, or the latex concentrated or non-concentrated may be used as a latex type adhesive. The isolated polymer may be used as a solid dry rubber. The latex may be widely used in the industrial field other than as an adhesive.

The solvent-soluble polychloroprene prepared according to this invention is quite effective in use as the basic polymer for adhesives.

Adhesives comprising polychloroprene as the base substance have excellent resistance to weathering. Since they have outstanding adhesive force at room temperature, they are widely used. However they have a disadvantage that when an adhered body is exposed to a high temperature, the adhesive softens and the adhered layers come off. The adhesive force at high temperatures can be improved by copolymerizing chloroprene with acrylic acid, etc., but such copolymers are unstable and liable to gel during storage.

Adhesives composed of polychloroprene as the base have the disadvantage that they generally have low adhesive force in the initial stage of adhesion, thus requiring a comparatively long period for acquiring stronger adhesive force.

On the other hand, a base polymer which would give high viscosity when processed in adhesives with the least amount of polymer, i.e. with a low concentration of polymer, is desired.

The adhesives composed of the polychloroprene produced according to this invention are improved in these respects as shown in the Examples below.

The adhesive force at high temperatures of the adhesives composed of the polymer of high molecular weight obtained according to this invention is higher than that produced according to the conventional methods, with their stability completely retained. Their softening temperature and the initial adhesive force can be improved to a greater extent than those of the adhesives composed of the polymer produced according to the conventional methods. Furthermore, one of the most remarkable effect is the possibility of increasing the solution viscosity to a great degree at a certain concentration of the adhesive.

Upon applying an adhesive, it is required to increase the solution viscosity above a certain value. This problem is solved by increasing the basic polymer content. But such solution of the problem results in loss from an economic viewpoint, and therefore a technique to increase the solution viscosity without increasing the content of the base polymer is required.

The chloroprene prepared according to this invention is completely solvent-soluble and moreover the intrinsic viscosity of the polymer is markedly high. Therefore, the viscosity of the adhesive prepared by dissolving this polymer is remarkably higher than that of the polymer of lower intrinsic viscosity prepared according to the conventional method of adding the chain transfer agent in a single quantity.

The adhesives of this invention may contain apart from the base polymer and solvent, the ingredients in use for general adhesives, that is, metal oxides, aging inhibitors and various resins.

It goes without saying that the polychloroprene according to this invention may be used not only as the so-called solvent type adhesives which are prepared by dissolving a solid polymer in solvent, but also as basic latex for the latex type adhesives.

The following Examples will better illustrate the nature of the present invention. However the invention is not intended to be limited to these Examples. The term "part" means "part by weight" unless otherwise indicated.

Example 1

One hundred parts of chloroprene and 0.030 parts of *n*-DDM were emulsified in 150 parts of water containing 3 parts of disproportionated rosin, 0.80 parts of sodium hydroxide, 0.80 parts of sodium salt of condensation product of formaldehyde - naphthalene sulfonic acid and 0.5 parts of sodium hydrogen sulfite. After the liquid was cooled to 10°C, the polymerization was started by adding a solution of potassium persulfate and sodium salt of anthraquinone - sulfonic acid.

During the reaction, when the conversion ratio reached 28% and 58%, each time 0.015 parts of *n*-DDM was added supplementarily. When the conversion ratio reached 69%, an emulsion mixture of *p*-tertiary butyl catechol and thioldiphenylamine was added, and the polymerization was stopped. Then, the unreacted monomer was removed under reduced pressure. The polymer was isolated from the resulting latex by lowering the pH to 7, continuously freezing in thin layers, accompanied by washing and drying.

The polychloroprene thus prepared had an intrinsic viscosity of 4.43 when measured at 30°C in toluene. This value is far higher than the maximum value 2.2 of the intrinsic viscosity at a 69% conversion ratio with the chain transfer added in a single quantity. This polymer was completely soluble in benzene or toluene and did not contain gel at all. This polymer was named Sample I, and the physical properties of an adhesive prepared from it is shown in Example 3.

Example 2.

The polymerization was carried out in the same way as in Example 1 except that the polymerization temperature was 40°C and the

final conversion ratio at which the polymerization was stopped was 61%. Thus, a sample was prepared by adding *n*-DDM by portions as follows:

	Conversion ratio	Parts of <i>n</i> -DDM added/100 parts of monomer
10	0%	0.070 (added before the polymerization)
15	33%	0.020
	48%	0.020

The intrinsic viscosity $[\eta]$ of the sample was 4.35 at 30°C in toluene. Such a polymer of high viscosity as the above sample is not attained by the conventional method of adding the transfer agent in a single quantity as seen from Fig. 2 of the case of the polymerization at 40°C. The polymer in this Example is named Sample II, and the physical properties of an adhesive prepared with it are shown in Example 3.

Reference 1.

The polymerization was carried out in the same way as in Example 1 except that 0.090 parts of *n*-DDM was introduced before the beginning of the polymerization and no addition was made during the reaction. The polymerization was made to proceed up to a conversion ratio of 69%. The intrinsic viscosity $[\eta]$ of the polymer was 2.2. This is considered to be substantially the highest value obtained by polymerizing at 10°C with a conversion ratio of 69% by the conventional method. The polymer in this reference is named Sample III.

Reference 2.

The polymerization was carried out in the same way as in Example 2 except that 0.18 parts of the chain transfer agent was added before the beginning of the polymerization and no further addition was made during the reaction. The polymerization was made to proceed up to a conversion ratio of 61%. The intrinsic viscosity of the polymer thus obtained was 2.7, which was about the highest viscosity obtained by polymerizing at 10°C with a conversion of 61% by the conventional method. The polymer in this reference is named Sample IV.

Example 3.

Solution viscosity, initial adhesive force, high temperature adhesive force and softening point of the polymers prepared in Examples 1 and 2, and Reference 1 and 2 were respectively measured in the following manner.

1) Solution viscosity.

The raw polymer in the intact state (without kneading with rollers, etc.) was dissolved in toluene to form a 10% solution, and the Brookfield viscosity was measured.

2) Initial adhesive force.

An adhesive of the following recipe was applied on canvas and pressed. After 3 hours, the measurement was made.

3) High temperature adhesive force.

An adhesive of the following recipe was applied on canvas and the strength against the peeling-off force was measured at 80°C.

4) Softening temperature.

The adhesion was made between aluminium and rubber. The temperature was gradually raised and the temperature at which the adhesive force decreases was measured. (Load: 500 g). The recipe of the adhesives.

Polymer	100	80
Styrenated phenol	2	
MgO	8	
ZnO	5	
Tertiary butyl phenol resin	30	
Solvent	toluene	85

The results of the measurement is shown in the following table.

Polymerization temperatures	10°		40°	
Polymerization method	Ex. 1	Ref. 1	Ex. 2	Ref. 2
Sample	I	III	II	IV
Solution viscosity cps.	83000	900	90000	2200
Initial Adhesive force (Kg/cm)	6.1	2.2	7.0	1.5
High temperature adhesive force (80°C) Kg/cm	4.3	1.1	5.1	1.5
Softening Temp. (°C) Load: 500g	above 150	86	above 150	69

Thus, it may be understood that all the polymers prepared according to this invention have very high solution viscosity, initial adhesive force, high temperature adhesive force and softening temperature compared with those of polymers prepared according to the conventional method. The most striking is that there is a relation between the solution viscosity and the intrinsic viscosity $[\eta]$ as shown in Fig. 3. Compared with the highest solution viscosity of about 2000 cps of the polymer obtained by the conventional method at a conversion ratio above 60%, the solution viscosity of the polymers prepared according to this invention is about 40 to 50 times. Further it is observed that there is a possibility of obtaining polymers having a solution viscosity of 400 to 500 times those of the conventional polymers.

Example 4.

The polymer was prepared in the same way as in Example 2 except that 100 parts of chloroprene monomer and 10 parts of styrene as a comonomer were used and the addition of *n*-DDM was made as follows:

0.05 parts, 0.02 parts and 0.01 part of *n*-DDM were added to 100 parts of chloroprene monomer, respectively before the polymerization, at the time of a 30% conversion ratio and at the time of 50% conversion ratio. The intrinsic viscosity of the resulting polymer in toluene was 4.15.

Example 5.

The polymer was prepared in the same way as in Example 2 except that 100 parts of chloroprene monomer and 10 parts of 2,3-dichloro 1,3 - butadiene was used and the addition of *n*-DDM was made as follows:

0.08 parts of *n*-DDM was added before the polymerization and 0.03 parts of it at the time of both 30% and 50% conversion ratio. The intrinsic viscosity of the resulting polymer was 4.05.

Example 6.

The sample prepared in Example 2 was roll-mixed according to the following recipe. The physical properties of the mixed compound and vulcanizate were measured. The results are shown below.

Recipe:

Polychloroprene of high viscosity	100	
Stearic acid	0.5	
Phenyl - α - naphthylamine	2	55
Magnesia (MgO)	4	
MT carbon black	500	
Process oil (Sundex No. 790, Sun Oil Co.)	120	
Zinc oxide (ZnO)	5	60
2-mercapto imidazoline	0.75	

Results:

Compound mooney (large rotor at 100°C)	42	
Scorch time (5 points rise at 121°C)	25 min.	65
Flow rate (Koka type flow tester, 100°C x 30 kg/cm ²)	106 x 10 ⁻³ cc/sec	

Vulcanizate (curing at 150°C, 20 min.)

Modulus at 100% elongation	40kg/cm ²	
Tensile strength	83kg/cm ²	70
Elongation	240%	
Hardness (JIS)	80	
Permanent set	5%	
Compression set	53%	
Tear strength	25kg/cm	75
Rebound (Schob)	13%	

From the above it may be understood that the rubber compound prepared with the polymer produced according to this invention has excellent properties.

5 WHAT WE CLAIM IS:—

1. A method of preparing polychloroprene comprising polymerizing chloroprene or a mixture of chloroprene with a copolymerizable monomer at a temperature of from 5° to 55° C wherein *n*-dodecyl mercaptan is present at the beginning of the polymerization reaction and further *n*-dodecyl mercaptan is added during the polymerization reaction in such a way as to prevent gel formation, at least 10 to 50% by weight of the total amount of *n*-dodecyl mercaptan being present at the beginning of the reaction.

2. A method as claimed in claim 1, wherein the further *n*-dodecyl mercaptan is added at least once during the polymerization reaction at a time before that at which gel formation would occur if the addition had not taken place.

3. A method as claimed in claim 1, wherein the further *n*-dodecyl mercaptan is added continuously during the polymerization reaction.

4. A method as claimed in any one of claims 1 to 3, wherein the copolymerizable monomer is styrene.

5. A method as claimed in any one of claims 1 to 3, wherein the copolymerizable monomer is 2,3 - dichloro - 1,3 - butadiene.

6. A method as claimed in claim 1 or 2, wherein the polymerization is started in the presence of 0.03 to 0.08 parts by weight of

n-dodecyl mercaptan for 100 parts of the monomer and during polymerisation, from a conversion ratio of 5 to 60%, a further 0.03 to 0.06 parts by weight of *n*-dodecyl mercaptan is added, the polymerisation being performed at a temperature from 10° to 20°C, the initial amount being at least 50% by weight of the total *n*-dodecyl mercaptan added.

7. A method as claimed in claim 1 or 2, wherein the polymerisation is started in the presence of 0.03 to 0.08 parts by weight of *n*-dodecyl mercaptan for 100 parts of the monomer and during polymerization, from a conversion ratio of 5 to 60%, a further 0.03 to 0.06 parts by weight of *n*-dodecyl mercaptan is added, polymerization being performed at a temperature from 20° to 55°C, the initial amount being at least 50% by weight of the total *n*-dodecyl mercaptan added.

8. A method of preparing a polychloroprene polymer or copolymer substantially as described in any one of Examples 1, 2, 4 or 5.

9. A polychloroprene polymer or copolymer whenever obtained by a process as claimed in any preceding claim.

10. A latex or solvent adhesive in which the base polymer is a polymer or copolymer as claimed in claim 9.

11. An adhesive as claimed in claim 10 substantially as described in Example 3.

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FIG. 1

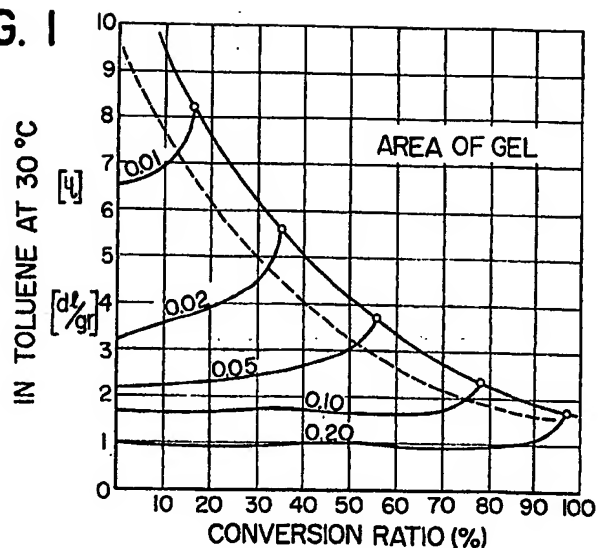


FIG. 2

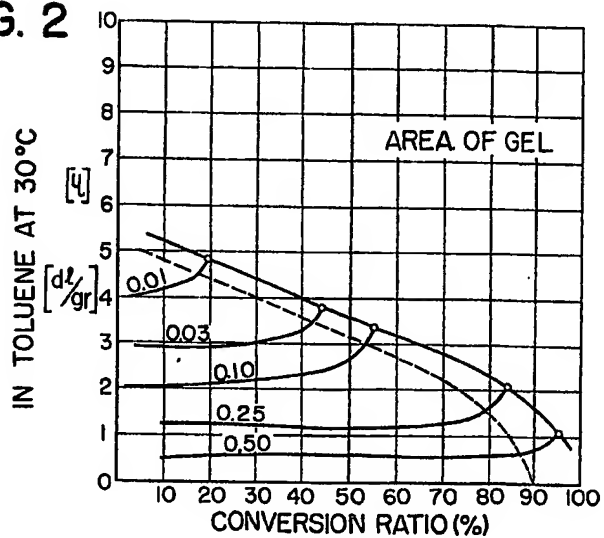


FIG. 3

